PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	:	
Wang et al.	:	
Application No. 10/036,332	:	Art Unit: 1724
Filed: Dec. 24, 2001	:	Examiner: R. Hopkins
For: CARBON NANOTUBE CONTAINING STRUCTURES, METHODS OF MAKING, AND PROCESSES USING SAME	:	Atty Docket: 12860E-CIP

DECLARATION PURSUANT TO 37 CFR § 1.131

1. The attached document in which the first line reads "Prepare two kinds of samples:" is a copy of six lab notebook pages that were all written by Yufei Gao before 20 September 2000. These notebook pages contain descriptions of experiments that were carried out before 20 September 2000.

2. As indicated on the third line of the first page, a goal of this work was to prepare a structure of $CoRu/Al_2O_3$ particles on carbon nanotube sponge grown on mesoporous $SiO_2/Fe/Al_2O_3$ dense coating/stainless steel foam.

3. The second page of the attachment shows an early experiment in which a coating of carbon nanotubes ("CN") was deposited on a stainless steel foam.

4. The sixth (and last) page of the attachment shows the successful synthesis of composite structures that included carbon nanotubes on a stainless steel foam.

5. The stainless steel foams used in this work had large pores and these foams had through porosity. The stainless steel foam had a pore size of more than 100 nm.

6. All of the attached documents have been copied without change except that dates have been blanked out.

7. The work in the attached notebook pages is that of Yufei Gao. At the time of the work described in the attached notebook pages, Dr. Gao was working with Yong Wang.

8. Claim 6 of the pending application states:

> A porous carbon nanotube containing structure comprising:
> a large pore support having through porosity; and
> carbon nanotubes disposed over the large pore support.

Yufei Gao and Yong Wang are joint inventors of claim 6. Ya-Huei Chin, Christopher L. Aardahl, and Terry L. Stewart are not joint inventors of the subject matter of claim 6.

9. I declare that all of the above statements made of my own knowledge are true and all statements made on information and belief are believed to be true. I understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. §1001), and may jeopardize the validity of the application or any patent issuing thereon.

Date: 5/18/04 By: _____
Yong Wang

Date: 5/19/04 By: _____
Ya-Huei Chin

Date: 5/12/04 By: _____
Yufei Gao

Date: 5/21/04 By: _____
Christopher L. Aardahl

Date: 5/21/04 By: _____
Terry L. Stewart

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Using colloidal Al_2O_3 particles to coat carbon nanotubes

Carbon nanotubes / metal foam
└ surf. area : ~ 1000 m^2/g

Three small pieces
#1, #2 — etching in 50% H_2SO_4 / 50% NH_3 for 10 min at room temp.
⇒ hydrophilic

#1 sample:
dip in 20% Al_2O_3 solution (original one)

#2 Sample:
dip in 50% ethanol / 50% - 0.5% Al_2O_3 solution

#3 Sample:
No chemical etching
dip in 0.2% Al_2O_3 solution

SEM image:
It appears that there is a dense layer on top of the CNT film.
#1 & #2 Samples have some cracks on the dense layer, &
#3 Sample has a high density of cracks — due to the hydrophobic nature?

It is not clear how much Al_2O_3 inside the CNT film for #1 & #3.
SEM shows a lot of Al_2O_3 on CNT tubes in the CNT film for Sample #3.

Note: Samples made on Dec.

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Try to dilute the $AlCl_3$ solution more in order to coat the CN film.

- #1 sample (small)
  etching in 50% H_2SO_4 / 50% HNO_3 for 10 min at RT
  Dip in 3:1 Ethanol : 10% $AlCl_3$ solution

- #2 sample (big)
  etching in 5% H_2SO_4 / 50% HNO_3 for 10 min at RT
  Dip in 4:1 Ethanol : 10% $AlCl_3$ solution

Both were fine. dried after spin

SEM (old one, new one also not yet work)
Both small & big samples still have a dense coating layer. SEM can't tell whether there is any $AlCl_3$ in the CN film due to poor resolution

⇒ Should I wash the sample in H_2O/EtOH after dip coating the $AlCl_3$ to remove any excess $AlCl_3$ particles on the top of CN film?

Note:
1) New SEM shows no dense layer on top of the CN film

2) It appears that 4:1 solution is better. Next I will fine tune the dip coat on CNS or is CN film

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Coat Co, Ru on Al_2O_3 / CN / Foams:

- Try to coat the foams in #2 Co/Ru solution
  ⇒ too much
  or at thickness ? testing

- Samples:
  Two colloid Al_2O_3 / Foams (small & big)
  One CVD Si-Al_2O_3 / Foam

- Initial weight & weight gain:
  CVD: 0.0246 ⇒ 0.0261 = 0.0015 g or 6%
  big (4:1): 0.0316 ⇒ 0.0348 = 0.0032 or 10%
  small (3:1): 0.0175 ⇒ 0.0194 = 0.0019 or 10%
  } after Dae. Drie

- SEM
  CVD:
  most CNs are still individual, & coatings are quite uniform (Co/Ru). CNs inside the pores appear smaller in diameter.
  Without Si during, the Al_2O_3 coating maybe just coat.
  Photo: C1211_1 ⇒ -8

  Big (4:1):
  Co/Ru / Al_2O_3 coatings appear very uniform (low mag)
  small Al_2O_3 particles (~20nm diameter) also fill the space between CNs (at least on out surface). Small pores can be ~~obtained~~ observed. C1215_1 ⇒ -4

  Small (3:1):
  The Co/Ru / Al_2O_3 coatings appear not as dense as the big (4:1)
  Large pores are clearly visible. C1214_1 ⇒ -7

The difference bet big & small may be due to the size effe
For small piece, the excess solution can be easily removed

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2. Yue Fei Gao Date _____

Prepare two kinds of samples:
1) Co Ru / Al_2O_3 mesoporous coating / Al_2O_3 dense coating / SS foam
2) Co Ru / Al_2O_3 particles / Carbon nanotube sponge / Mesoporous Al_2O_3 / Al_2O_3 dense coating / SS;

- First Al_2O_3 dense coatings on SS foam
  4 Monoliths of SS foams from Ryan (this morning)
  Al_2O_3 coatings:
  - 700°C growth temperature
  - 102°C Al bubbler temperature (64%) } took 3 hrs to stabilized
  - 151°C Line temperature (56%) }
  - Heating to 700°C in 600sccm N_2, 5°C/min
  - growth:
    Air – 600sccm,
    Al carrier: 30sccm 5.8% output
    20 min growth time
    5 Torr
  - cooling down to RT (off power) in N_2

initial weight: 0.2800 g | 0.2601 g (flow)
0.28558 g | 0.26029 g

After growth: 0.2800 g | 0.2601
0.2820 g | 0.2611
gain 0.0020 g | 0.0010 g
0.2858 | 0.2602
0.2872 | 0.2622
0.0014 g | 0.0020 g

- Al_2O_3 mesoporous coatings
  Solution #1
  1.5 g H_2O, 4g EtOH, 0.08 g HCl, 1 g $C_{16}EO_{10}$, 1.0 g AIO
  ⇒ did not use because of H_2O!
  Solution #2
  5.5 g EtOH, 0.08 g HCl, 1 g $C_{16}EO_{10}$, 1.0 g $AlCl_3$
  0.2622 → 0.2700 ⇒ 0.0078 g gain ⇒ looks good!
  Solution #3
  5 g EtOH, 0.25 g P123, 0.8 g $AlCl_3$
  0.2820 → 0.2980 ⇒ 0.0164 g ⇒ too much on surface!
  ↳ too much ⇒ due to P123!

Calcined at 500°C for 1 hr 500 Torr, 1000sccm air

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- Carbon Nanotube Seed layer
Solution # 4
1.5 g H_2O, 4 g EtOH, 0.08 g HCl. 2 g C580..., 4 ml ?.
Two monoliths:

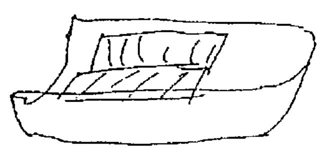
Calcined at 500°C for 1 hr in 1000 sccm Air 500 torr

0.2611 → 0.2720 → 0.0109 g } Both look quite uniform, no
0.2872 → 0.2976 → 0.0104 g } cracks on the surfaces
Also:
dip coating ~ 10 small foams coated with Al_2O_3/SiO_2 previously.
Most are ... Olices
⇒ see some bubbles on the external surface, which were absent without $Fe(NO_3)_3 \cdot 6H_2O$
Two dried on a hot plate ⇒ more bubbles on the surface
Also coated ~10 flat SS sampled

- Carbon Nanotube growth

done

Flow
→



#② see SEM images
L1256-1, -2

500 sccm N_2 atmosphere
350°C/hr → 750°C 500 sccm N_2
at 750°C, 900 sccm ethylene for 5 min ⇒ 300 sccm for 25 min
350°C/hr → RT, 500 sccm N_2

⇒ Too much Carbon Nanotubes!
I used wrong time, last time growth time was 10 min, not 30 min!
⇒ Carbon Nanotubes almost completely filled the pores!
L ~ 10 μ by

Weight gain:
0.2858 g → 0.2872 → 0.2976 → 0.003 → 0.1437 CN
Foam CVD Fe/SiO2 CN
⇒ almost complete filled

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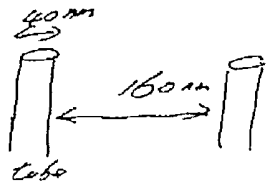
- Al_2O_3 particle Deposition on Carbon Nanotubes

Solution method:

$AlCl_3$ $d = 2.44$ g/cm³



Solution vol.: $\pi(100^2 - 20^2) \cdot 1$ (unit length) $= 9600\pi$

filled with solution

$AlCl_3$ coating δ – thickness

$2\pi r\delta \cdot 1 = 40\pi \cdot \delta$

Thus. 10 vol% $AlCl_3$ in solution:

$9600\pi \cdot 10\% = 40\pi \cdot \delta \Rightarrow \delta = \frac{96}{4} = 24$ nm

making 10 wt.% $AlCl_3$ in EtOH:

5 ml EtOH

10% → 0.5 ml $AlCl_3$ → $0.5 \times 2.44 = 1.22$ g $AlCl_3$

when mixing $AlCl_3$ in 5 ml EtOH, generating a lot of heat! the glass bottle was hot.

This was done in the glove box.

Notes:

The solution was stirred over weekend with the cap closed

⇒ very thick colloid solution, why?

– forming Al ethoxide? $Al(OC_2H_5)_3$ particles?

making a TEM sample, diluting the colloid solution by a factor of ~2 (4 ml EtOH)

⇒ completely dissolved. No precipitations!

No TEM samples.

Take out 4 ml solution, & add 0.6 g Al_2O_3 ⇒ ~10%

⇒ colloid! add all EtOH: 9 ml at $1.22 \times 1.5 = 1.82$ g $AlCl_3$

Thickness too much!

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